

**3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (1).** Electrolysis of the Diels-Adler adduct of 6,6-dimethylcyclohexadienone<sup>13</sup> and maleic anhydride by using the procedure reported by Luibrand and Fujinari<sup>12</sup> resulted in the bicyclic ketone 1: UV max (95% C<sub>2</sub>H<sub>5</sub>OH) 212 nm ( $\epsilon$  3700), 230 (sh, 832), 297 (40). Deuterium-labeled ketone 4<sup>12</sup> was prepared by exchange of hydrogens of the adduct by using deuterium oxide and sodium deuterioxide heated to 150 °C for 24 h in a stainless-steel bomb calorimeter, prior to the electrolysis. The deuterium analysis<sup>17</sup> of the resulting dicarboxylic acid is as follows: calcd for exchange of two hydrogens, 16.67% excess deuterium; found, 13.17%, corresponding to 79% incorporation of two deuterium atoms.

**Direct Irradiation of 3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (1).** A solution of 0.63 mg of ketone 1 in 5 mL of ether in a quartz tube was irradiated with a 450-W, Hanovia, medium-pressure lamp fitted with a Vycor filter. GLC (FFAP) analysis after 75 min revealed that most of the starting material had reacted, and only peaks at very short retention times were present. None of the tricyclic ketone 6 formed.

**Photorearrangement of 3,3-Dimethylbicyclo[2.2.2]octa-5,7-dien-2-one (1).** A solution of 0.49 g (3.3 mmol) of 3,3-dimethylbicyclo[2.2.2]octadien-2-one in 36 mL of acetone was placed in a quartz tube and degassed by bubbling nitrogen through the solution for 1 h. The tube was irradiated at room temperature with a 450-W, Hanovia, medium-pressure lamp fitted with a Vycor filter. Aliquots were analyzed by GLC (FFAP or di-*n*-decyl

phthalate) and indicated the formation of a number of peaks with short retention times (one of which corresponded to the retention time of benzene), a primary photoproduct (6), and an unidentified product which formed upon continued irradiation of 6. GLC retention times (di-*n*-decyl phthalate, 0.64 cm  $\times$  3 m, 120 °C, He flow rate 60 mL/min) were as follows: starting ketone 1, 35 min; unidentified secondary photoproduct, 33 min; tricyclic ketone 6, 59 min. (A control experiment in which pure 6 was irradiated under the same conditions confirmed that the unidentified product was formed from 6.)

After 16 h of irradiation, the solution was concentrated, and the products were isolated by preparative GLC (FFAP, 0.96 cm  $\times$  6 m, 150 °C, He flow rate 250 mL/min). Some starting ketone 1 (6.3 mg, retention time 43 min) was recovered, in addition to 48 mg (10%) of 4,4-dimethyltricyclo[3.3.0.0<sup>2,8</sup>]oct-6-en-3-one (6, retention time 106 min) as a colorless liquid: IR (neat) 3030 (w), 2940 (m), 2905 (m), 1620 (s, carbonyl), 1590 (w), 1465 (m), 1376 (m), 1359 (m), 1342 (m), 1299 (m), 1087 (m), 893 (m), 747 (m) cm<sup>-1</sup>; NMR, see text and structure 6 for results; mass spectrum, *m/e* 148, 133, 70, 42; UV max (95% C<sub>2</sub>H<sub>5</sub>OH) 202 nm ( $\epsilon$  7300), 233 (sh,  $\epsilon$  1500). Anal. Calcd for C<sub>10</sub>H<sub>12</sub>O: C, 81.04; H, 8.16. Found: C, 80.82; H, 7.94. Purification of deuterated 6 from irradiation of 4 was carried out using a di-*n*-decyl phthalate GLC column. NMR results are shown in Table I.

Registry No. 1, 55693-20-4; 4, 76756-38-2; 6, 76756-39-3.

## Aspects of Selective Oxidation and Ammoxidation Mechanisms over Bismuth Molybdate Catalysts. 3. Substituent Effects in the Selective Oxidation of Allylbenzenes<sup>1</sup>

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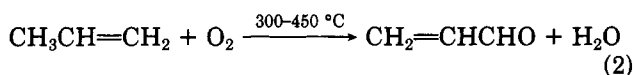
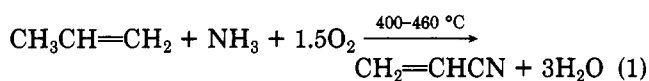
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The relative rates of catalytic oxidation of *p*-XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub> (X = H, CH<sub>3</sub>, Cl, OCH<sub>3</sub>) at 320 °C over MoO<sub>3</sub>, Bi<sub>2</sub>MoO<sub>6</sub>, Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>, and a multicomponent system (M<sub>a</sub><sup>2+</sup>M<sub>b</sub><sup>3+</sup>Bi<sub>x</sub>Mo<sub>y</sub>O<sub>z</sub>) have been determined at low (<2.5%) conversion. The relative rates for the bismuth-containing catalysts are 1.00 (H), 1.55 (CH<sub>3</sub>), 1.98 (Cl), and 3.03 (OCH<sub>3</sub>), while for MoO<sub>3</sub> the values are 1.00 (H), 1.78 (CH<sub>3</sub>), 1.38 (Cl), and 3.42 (OCH<sub>3</sub>). The main products of the reaction under these conditions are cinnamaldehyde and indene, while increasing amounts of CO and CO<sub>2</sub> are also produced at higher conversions. Relative cinnamaldehyde selectivity decreases with increasing electron-donating ability of X (Cl > H > CH<sub>3</sub> > OCH<sub>3</sub>) and decreasing Bi content in the catalyst (Bi<sub>2</sub>MoO<sub>6</sub> > Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> > MoO<sub>3</sub>). The results are interpreted in terms of the formation of a radical-like phenylallyl-molybdenum surface  $\pi$  complex in the rate-determining step and, subsequently, the corresponding  $\sigma$ -O molybdate complex which is the intermediate for both cinnamaldehyde and indene formation. These results strongly suggest that in the selective oxidation of propylene over bismuth molybdate catalysts the  $\pi$ -allylic surface complex formed in the rate-determining step is radical-like in character.

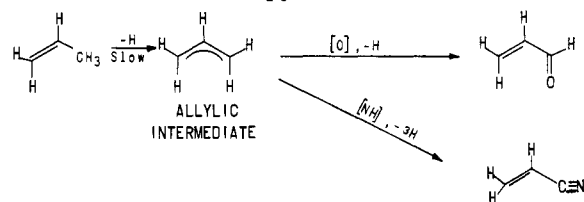
### Introduction

Since its discovery some 2 decades ago, the selective ammoxidation (eq 1) and oxidation (eq 2) of propylene by



heterogeneous catalysis has become of major industrial

### Scheme I. Selective Propylene Oxidation Mechanism



importance. The simple bismuth molybdates, Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> ( $\alpha$ ), Bi<sub>2</sub>Mo<sub>2</sub>O<sub>9</sub> ( $\beta$ ), and Bi<sub>2</sub>MoO<sub>6</sub> ( $\gamma$ ) can function in both processes and are the best known and most extensively studied systems. They also serve as the basis for many of today's highly active and selective multicomponent industrial catalysts.

The most well-accepted feature of the mechanism for propylene ammoxidation and oxidation<sup>1,2</sup> is the formation

(1) (a) Part II of this series: Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Catal.* 1980, 63, 235 and references therein. (b) Preliminary communication of Part III: Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Catal.*, in press. (c) Presented at the Second North American Chemical Congress, Las Vegas, NV, Aug 28, 1980.

Table I. Catalyst Properties

composition	density, g/cm <sup>3</sup>	surface area, m <sup>2</sup> /g
MoO <sub>3</sub>	1.9	0.7
Bi <sub>2</sub> Mo <sub>3</sub> O <sub>12</sub>	1.2	2.9
Bi <sub>2</sub> MoO <sub>6</sub>	1.9	3.6
M <sub>a</sub> <sup>2+</sup> M <sub>b</sub> <sup>3+</sup> Bi <sub>x</sub> Mo <sub>y</sub> O <sub>z</sub>	0.92	6.5

of an allylic intermediate in the rate-determining step via  $\alpha$ -hydrogen abstraction<sup>3,10</sup> (Scheme I). The fast subsequent steps must involve O (or NH insertion if ammonia is present) and hydrogen abstraction to form acrolein or acrylonitrile, respectively. While the nature of this intermediate remains controversial, for bismuth molybdate catalysts, experimental evidence is more consistent with the formation of a cationic or radical-like species as opposed to an anionic allylic intermediate.<sup>4,5,10</sup>

A classical physical-organic method for determining the nature and magnitude of charge in transition states is the use of the Hammett equation. While most Hammett studies deal with stoichiometric homogeneous reactions carried out at temperatures less than 100 °C, linear correlations have been found for several heterogeneous catalytic systems, including acid-catalyzed cracking and dehydration reactions<sup>6</sup> and catalytic hydrogenation of cyclohexanones,<sup>7</sup> methylenecyclohexanes,<sup>8</sup> and methyl-substituted benzenes.<sup>9</sup>

The effect of alkyl substituents for the oxidation of a series of aliphatic olefins over a bismuth molybdate catalyst at 460 °C has been studied by Adams,<sup>10</sup> who found that olefin relative reactivities are related to the type of allylic hydrogen abstracted, following the order: tertiary (75) > secondary (14) > primary (1). In addition, a good linear correlation was found between the rate of catalytic olefin oxidation and allyl hydrogen abstraction by *tert*-butoxy radicals in solution. These data suggest formation of either an allylic radical species or one which has some cationic character, since carbonium ion formation would give the same ordering of rates but would span a range of 10<sup>8</sup> rather than the 10<sup>2</sup> observed.

This work describes the determination of relative oxidation rates of a series of *p*-substituted allylbenzenes (*p*-

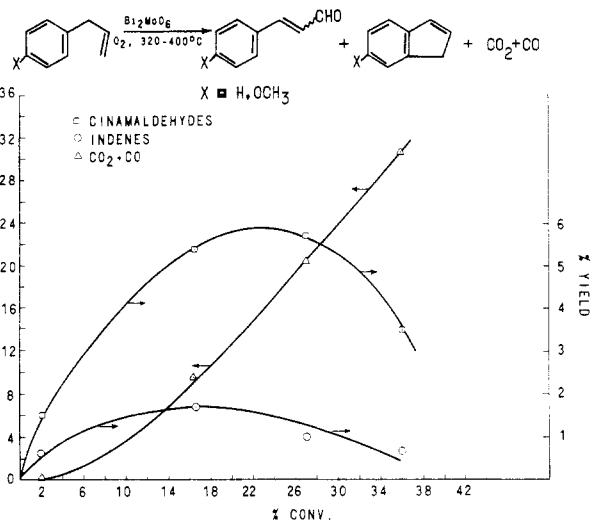
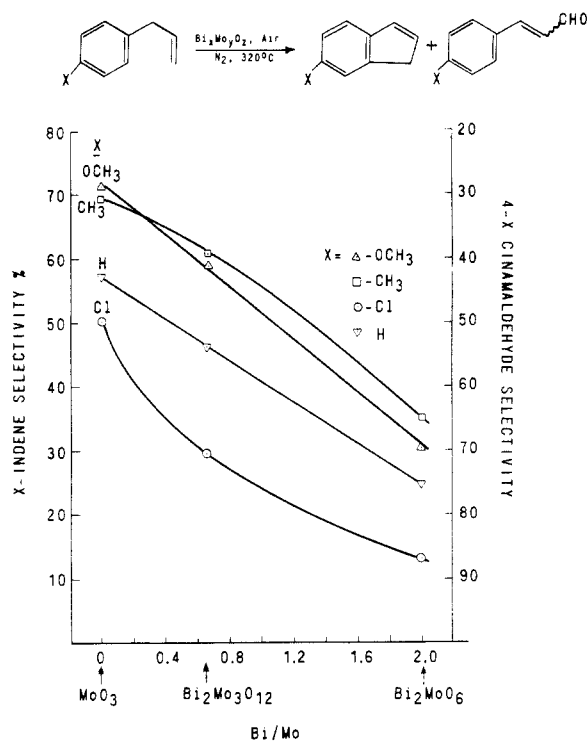


Figure 1. Product distribution vs. allylbenzene conversion.

Figure 2. Indene selectivity-catalyst effect for catalytic oxidation of *p*-X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub> at 320 °C, 0.4 s.

XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub>, where X = Cl, H, CH<sub>3</sub> and OCH<sub>3</sub>) over MoO<sub>3</sub>, Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>, Bi<sub>2</sub>MoO<sub>6</sub>, and a multicomponent system, M<sub>a</sub><sup>2+</sup>M<sub>b</sub><sup>3+</sup>Bi<sub>x</sub>Mo<sub>y</sub>O<sub>z</sub>. In analogy to the oxidation of propylene to acrolein, previous studies indicate that cinnamaldehyde, the expected selective oxygen insertion product, is formed in heterogeneous catalytic oxidation of allylbenzene.<sup>11a</sup> Likewise, catalytic oxidation or ammoxidation of  $\alpha$ -methylstyrene gives the expected atropaldehyde or atropnitrile, respectively.<sup>11b</sup>

## Experimental Section

**Materials.** Catalysts (20–35 mesh) were unsupported, prepared as previously described,<sup>4</sup> and had the properties listed in Table I.

Allylbenzene (Aldrich), *p*-allyltoluene (ICN), *p*-allylanisole (MCB), and *p*-allylchlorobenzene, obtained from the reaction of

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(6) Kraus, M. *Adv. Catal.* 1967, 17, 94. Kraus, M.; Kochloeff, K. *Collect. Czech. Chem. Commun.* 1967, 32, 2320. Kraus, M. *Ibid.* 1969, 34, 699.

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(8) Taya, K.; Morimoto, S.; Abe, C.; Nomura, K.; Nomura, O.; Tanaka, K. *Bull. Chem. Soc. Jpn.* 1980, 53, 1034.

(9) Smith, H. A.; Campbell, W. E. Proceedings of the Third International Congress on Catalysis, Amsterdam, 1964; North Holland Publishers: Amsterdam, 1965; p 1373.

(10) Adams, C. L., ref 9, p 240.

(11) (a) Grasselli, R. K. [Standard Oil Co. (Ohio)] U.S. Patent 3 452 032, June 24, 1969. (b) Grasselli, R. K.; Burrington, J. D.; Suresh, D. D.; Friedrich, M.S.; Hazle, M. A. *S. J. Catal.*, in press.

Table II. Catalytic Oxidation of a 1:1 Mixture of  $p\text{-XC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{CH}_2^a$ 

X	catalyst <sup>b</sup>	temp, °C	C.T., s <sup>c</sup>	% unreacted X			% yield						
				AB	$\Sigma^d$	$p\text{-X-AB}$	CA	$\Sigma^e$	X-CA	IN	$\Sigma^f$	$p\text{-X-IN}$	CO + CO <sub>2</sub>
OCH <sub>3</sub>	MoO <sub>3</sub>	320	0.4	99.2		97.1	0.46		0.65	0.30		2.29	0.0
	MoO <sub>3</sub>	320	0.8	98.6		95.2	0.85		1.63	0.58		3.16	0.0
	Bi <sub>2</sub> Mo <sub>3</sub> O <sub>12</sub>	320	0.4	98.7		96.2	0.80		1.55	0.47		2.24	0.0
	Bi <sub>2</sub> MoO <sub>6</sub>	320	0.4	98.9		96.7	0.89		2.30	0.21		1.02	0.0
	Bi <sub>2</sub> MoO <sub>6</sub>	380	0.37		83.4			5.4			1.7		9.5
	Bi <sub>2</sub> MoO <sub>6</sub>	400	0.35		72.9			5.7			1.0		20.4
	M.C.	320	0.4	98.5		95.4	0.81		1.60	0.64		2.99	0.0
	M.C.	320	0.8	97.8		93.9	1.25		2.65	1.88		3.49	0.0
	Bi <sub>2</sub> MoO <sub>6</sub>	400	0.7		63.9			3.5			0.69		30.7
	Cl	MoO <sub>3</sub>	320	0.4	99.3		99.0	0.14		0.46	0.54		0.52
MoO <sub>3</sub>		320	0.8	98.6		98.2	0.46		0.97	0.93		0.87	0.0
Bi <sub>2</sub> Mo <sub>3</sub> O <sub>12</sub>		320	0.4	98.6		97.4	0.68		1.82	0.72		0.77	0.0
Bi <sub>2</sub> MoO <sub>6</sub>		320	0.4	98.2		96.4	1.30		3.16	0.45		0.48	0.0
M.C.		320	0.4	97.3		94.9	1.18		3.43	1.55		1.66	0.0
M.C.		320	0.8	96.2		92.3	1.62		5.50	2.21		2.15	0.0
CH <sub>3</sub>	MoO <sub>3</sub>	320	0.8	98.7		97.8	0.54		0.68	0.72		1.55	0.0
	Bi <sub>2</sub> Mo <sub>3</sub> O <sub>12</sub>	320	0.4	98.7		97.9	0.63		0.82	0.66		1.28	0.0
	Bi <sub>2</sub> MoO <sub>6</sub>	320	0.4	98.2		97.4	1.26		1.75	0.58		0.95	0.0
	M.C.	320	0.4	98.1		96.9	0.77		0.92	1.17		2.16	0.0
	M.C.	320	0.8	96.7		95.4	1.58		1.61	1.75		3.02	0.0

<sup>a</sup> Total olefin-air-N<sub>2</sub> for all runs = 1:15:78; AB = allylbenzene, CA = cinnamaldehyde, IN = indene. <sup>b</sup> M.C. = multi-component system: M<sub>a</sub><sup>2+</sup>M<sub>b</sub><sup>3+</sup>Bi<sub>x</sub>Mo<sub>y</sub>O<sub>z</sub>. <sup>c</sup> Catalyst volume = 1.25 cm<sup>3</sup> (0.4 s) and 2.50 cm<sup>3</sup> (0.8 s) at 320 °C, C.T. = contact time. <sup>d</sup>  $\Sigma$  AB +  $p\text{-X-AB}$ . <sup>e</sup>  $\Sigma$  CA +  $p\text{-X-CA}$ . <sup>f</sup>  $\Sigma$  IN +  $p\text{-X-IN}$ .

*p*-chlorophenyl magnesium bromide with allyl bromide,<sup>13</sup> were run through a column of activated alumina (1 g/8 g of olefin purified) before use. Authentic samples of indene (Aldrich) and cinnamaldehyde (MCB) were used without further purification. Substituted cinnamaldehydes,  $p\text{-XC}_6\text{H}_4\text{CH}=\text{CHCHO}$  (X = CH<sub>3</sub>, OCH<sub>3</sub>, Cl) (used as authentic samples), were prepared by reaction of a 0.2:1.0:2.2 (molar) mixture of NaOH,  $p\text{-XC}_6\text{H}_4\text{CHO}$ , and acetaldehyde, respectively, in 16% ethanol/water solution.<sup>12</sup> Tetrahydrofuran (Aldrich) was distilled from LAH prior to use to remove inhibitor (BHT).

**Catalytic Oxidation Procedure.** Each equimolar mixture of allylbenzene and *p*-substituted allylbenzene was injected via syringe pump into an air/N<sub>2</sub> mixture and vaporized in the pre-heated zone of a single-pass, plug-flow, tubular stainless-steel microreactor (volume 5 mL, diameter 0.95 cm) operated under atmospheric pressure at 320–400 °C. The feed was a 1:15:78 (molar) mixture of allylbenzene-air-N<sub>2</sub>; the gas composition was controlled by a mass flow controller. The products were collected for 30–60 min after a 5-min prerun, in two ice-cooled scrubbers, each containing 3 cm<sup>3</sup> of THF and *n*-C<sub>24</sub>H<sub>50</sub> as internal standard. Other reaction parameters are listed in Table II and Figures 1 and 2.

**Analysis.** Quantitative vapor-phase chromatographic analysis of the reaction scrubber solutions was performed on a 305 × 0.32 cm stainless-steel Super Pak 20M (Analabs, Inc.) column in a Varian 3760 gas chromatograph equipped with a flame-ionization detector and a He carrier gas (16 cm<sup>3</sup>/min), using the following temperature program: 100 °C (initial temperature) for 5 min, heated at 30 °C/min to 210 °C (*p*-allylchlorobenzene and *p*-allylanisole runs) or 230 °C (*p*-allyltoluene runs). Under these conditions, *cis*- and *trans*-cinnamaldehyde are not resolved. Thus, all cinnamaldehyde yields are reported in terms of the total (*cis* + *trans*). Each indene and cinnamaldehyde was collected by preparative gas chromatography and identified by comparison of NMR spectra and GC properties with authentic samples or, in the case of substituted indenenes, GC/mass spectral analyses.

No thermal decomposition of allylbenzenes was detected at 320 °C in control experiments using fused quartz.

## Results

**Product Distribution vs. Conversion.** The oxidation of allylbenzene over the selective oxidation catalysts gave the expected cinnamaldehyde, along with indene and, at

conversions greater than 2.5%, carbon oxides (mainly CO<sub>2</sub>, Table II). The change in product distribution with total allylbenzene conversion for the reaction of the *p*-methoxyallylbenzene/allylbenzene pair over Bi<sub>2</sub>MoO<sub>6</sub> is shown in Figure 1. Indene and cinnamaldehyde yields have maxima at about 18 and 22% conversion, respectively, while carbon oxides continue to rise over the entire conversion range investigated. However, if the conversion level is kept below 2.5%, indene and cinnamaldehyde are virtually the only products observed. Material balances under these conditions (320 °C, 0.4 s) are in general 95–105%. Only small amounts (<1% of the products) of isomerization to  $\alpha$ -methylstyrene, C–X cleavage, or double-bond oxidation were observed at this low conversion. Thus, in order to eliminate CO<sub>2</sub> complication, all subsequent pair-wise experiments were performed at conversions <2.5%.

**Product Distribution vs. Catalyst Composition.** Incorporation of bismuth (the allylic hydrogen abstracting component) into the catalyst results in decreased selectivity (yield/allylbenzene conversion) to indene and, thus, increased selectivity to cinnamaldehyde (Figure 2). Catalyst acidity also decreases with increasing Bi concentration.<sup>1</sup>

**Product Distribution vs. Hammett Substituent Constant.** The selectivity of substituted indene formation is increased by electron-donating groups (OCH<sub>3</sub>, CH<sub>3</sub>) and decreased by the electron-withdrawing group (Cl) relative to the average value for unsubstituted indene selectivity. For a given pair-wise run, log (X-indene selectivity/indene selectivity) is constant, regardless of catalyst. A Hammett plot of this value vs.  $\sigma$  gives a straight line ( $r = 0.98$ ) with a slope of  $-0.87$  (Figure 3). This correlation does not hold if yields are substituted for selectivities in this plot.

## Discussion

**Mechanism of Indene Formation.** Cinnamaldehyde results from rate-determining allylic hydrogen abstraction, in analogy to the mechanism of acrolein formation from propylene (Scheme I). The formation of indene, however, could occur by several reaction paths. From the results in Figures 2 and 3, which show that electron-donating

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(13) Frisch, K. C. *J. Polym. Sci.* 1959, 41, 365.

## Scheme II. Mechanism of Allylbenzene Oxidation

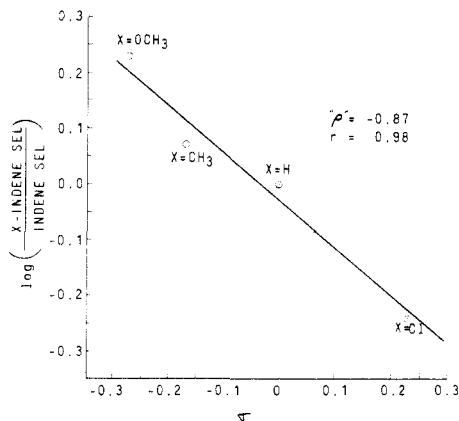
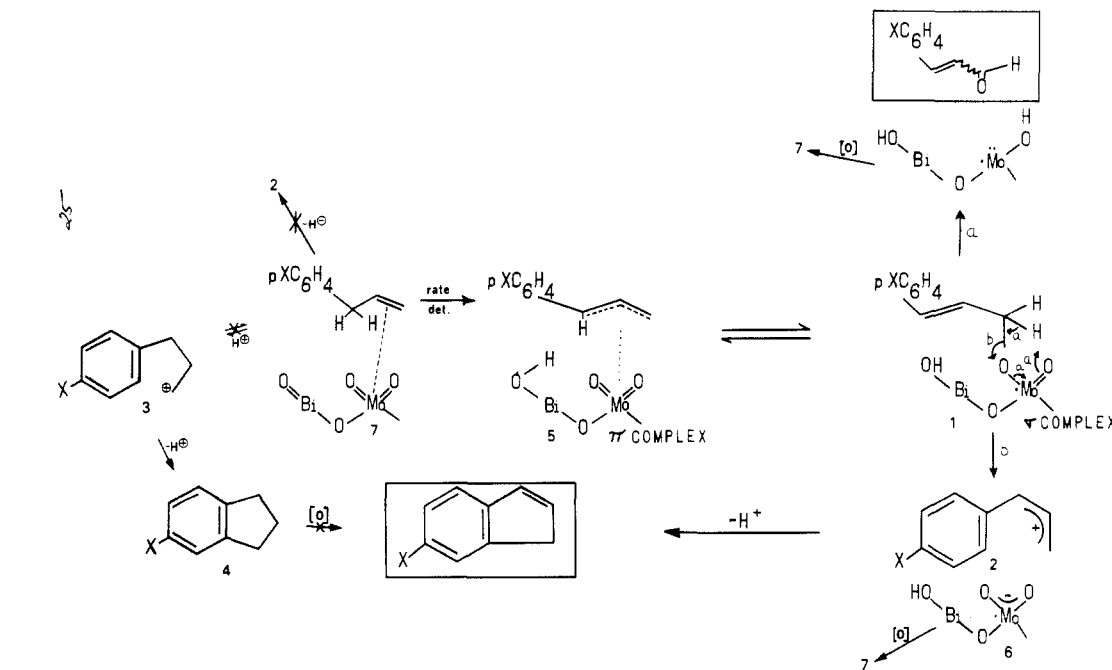


Figure 3. Indene formation—substituent effects.

groups increase relative indene selectivity, the formation of a cationic intermediate seems likely. Three probable mechanisms are shown in Scheme II. The first involves the same rate-determining step as for cinnamaldehyde formation, namely, allylic hydrogen abstraction, followed by formation of a  $\sigma$ -allylmolybdate 1, analogous to the acrolein precursor in propylene oxidation.<sup>1</sup> Heterolytic C–O cleavage forms 1-arylallyl carbonium ion 2, which results in 6-substituted indene after ring closure and proton loss. Ring closure of such aromatic allyl cations to form indene derivatives is a well-documented reaction.<sup>14</sup> Two alternate routes involve formation of cinnamaldehyde and indene by parallel routes. Direct formation of 2 via allylic hydride abstraction, or cyclization of primary carbonium ion 3 with subsequent oxidation of indan 4 also result in indene formation. Both of these routes have been proposed previously for the formation of methylindene and methylindan from the reaction of *n*-butylbenzene over metal catalysts.<sup>14</sup>

However, for several reasons, we suggest that formation of indene and cinnamaldehyde via the common allylic species 1 is the most likely mechanism. First, the route via 3 can be eliminated since, under the reaction condi-

Table III. Relative Reactivities ( $R_X/R_H$ ) for Selective Oxidation of  $p$ -X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub> at 320 °C

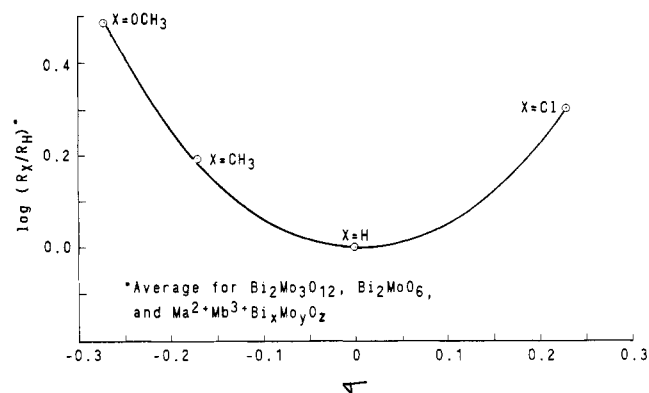
X	Bi <sub>2</sub> - Mo <sub>3</sub> O <sub>12</sub>	Bi <sub>2</sub> - MoO <sub>6</sub>	M <sub>a</sub> <sup>2+</sup> M <sub>b</sub> <sup>3+</sup> - Bi <sub>x</sub> Mo <sub>y</sub> O <sub>z</sub>	av	MoO <sub>3</sub>
H	1.00	1.00	1.00	1.00	1.00
CH <sub>3</sub>	1.65	1.48	1.51	1.55	1.78
Cl	1.86	2.11	1.97	1.98	1.38
OCH <sub>3</sub>	3.03	3.05	3.00	3.03	3.42

tions, no indan is converted to indene, and no indan is detected in the allylbenzene oxidation experiments. The formation of 2 by a rate-determining step different from that which forms cinnamaldehyde, i.e., by direct hydride abstraction, is unlikely since only relative indene selectivities, not relative indene yields, correlate with  $\sigma$  substituent constants. Correlation with yields would be expected if 2 were formed in the rate-determining step directly from allylbenzene. Furthermore, while the addition of pyridine to the gas-phase feed mixture reduces the selectivity to indene, there is no change in overall allylbenzene conversion, suggesting a common intermediate for both indene and cinnamaldehyde formation.

Thus, the relative reactivities ( $R_X/R_H$ ) of  $p$ -substituted allylbenzenes, which include both chemisorption coefficient ( $K$ ) and chemical rate constant ( $k$ ) terms, can be calculated from the conversions of allylbenzene and substituted allylbenzene in any pair-wise run, using eq 3. The use of the allylbenzene series with substituents in the para position is intended to minimize rate differences due to changes in chemisorption characteristics caused by steric effects.

$$\frac{R_X}{R_H} = \frac{k_X K_X}{k_H K_H} = \frac{\log [AB/AB_0]}{\log [(AB - X)/(AB - X)_0]} \quad (3)$$

**Relative Reactivities.** For the bismuth-containing catalysts (i.e., Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>, Bi<sub>2</sub>MoO<sub>6</sub>, and the multicomponent system), the relative reactivities for any one substituent X were the same, within  $\pm 5\%$  of the average (Table III), and decreased in the order X = OCH<sub>3</sub> (3.03) > Cl (1.98) > CH<sub>3</sub> (1.55) > H (1.00). These rate enhancements are much smaller than those expected for the formation of an ionic allylic intermediate. Furthermore, these data result in a U-shaped Hammett plot (Figure 4),



**Figure 4.** Relative reactivities ( $R_X/R_H$ ) for catalytic oxidation of  $p\text{-X-C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$  at 320 °C vs. Hammett substituent constant  $\sigma$ .

**Table IV.** Substituent Effects in Selective Oxidation. Relative Rates at 320 °C

$$p\text{-XC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2 \xrightarrow[320\text{ }^\circ\text{C, -H}\cdot]{\text{Bi}_x\text{Mo}_y\text{O}_z, \text{O}_2} p\text{-XC}_6\text{H}_4\text{CH}=\text{CH}-\text{CH}_2$$

$$[p\text{-XC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{N}]_2 \xrightarrow{\Delta, -\text{N}_2} 2p\text{-XC}_6\text{H}_4\text{CH}(\text{CH}_3)^{\cdot 17}$$

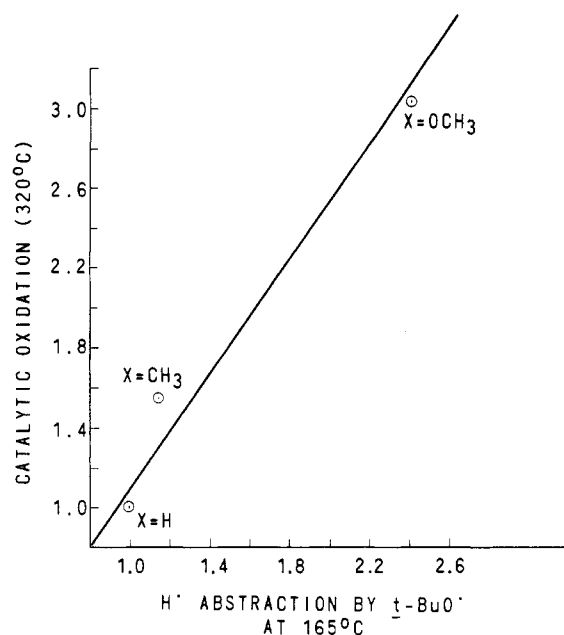
X	selective oxidn, $R_X/R_H$	azo decompn, $k_X/k_H$
H	1.00	1.00
CH <sub>3</sub>	1.55	1.18
Cl	1.98	2.43
OCH <sub>3</sub>	3.03	1.34

since both electron-withdrawing and -donating groups accelerate the reaction.

The observed behavior is more indicative of a radical rather than an ionic intermediate as shown by the small substituent effects for decomposition of benzyl azo<sup>15</sup> and azoxy<sup>16</sup> compounds. A small rate enhancement for electron-donating and -withdrawing groups is a general feature of both catalytic oxidation and radical-forming azo nitrogen extrusion<sup>17</sup> reactions (Table IV). In addition, a correlation is obtained between the relative rate of catalytic oxidation and that for allylic hydrogen abstraction by *tert*-butoxy radicals in solution at 165 °C<sup>18</sup> (Figure 5).

For MoO<sub>3</sub>, the relative rate ordering is OCH<sub>3</sub> (3.42) > CH<sub>3</sub> (1.78) > Cl (1.38) > H (1.00). Furthermore, relative rates for the electron-donating groups (OCH<sub>3</sub>, CH<sub>3</sub>) are higher than the average for the bismuth-containing catalysts, but lower than this average for the electron-withdrawing group Cl. This is indicative of an allyl cation forming component (i.e., H<sup>+</sup> abstraction) in the rate-determining step with MoO<sub>3</sub>, which is also consistent with the higher acidity and selectivity to indene (resulting from phenylallyl cation ring closure) for MoO<sub>3</sub>.

Also, as expected, the rate of reaction is slower for propylene than allylbenzene, since a 1:1 olefin mixture produces no acrolein, but only allylbenzene oxidation products—cinnamaldehyde and indene at 320 °C under the conditions of the other pair-wise experiments (Table III).



**Figure 5.** Comparison of the relative reactivity of  $p\text{-X-C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2$  in the catalytic oxidation over bismuth molybdates at 320 °C to that of allylic H-abstraction by *t*-BuO<sup>·</sup> at 165 °C.<sup>18</sup>

**Mechanism of Catalytic Oxidation.** On the basis of these results and those of previous studies,<sup>1,4</sup> an overall mechanism can be formulated (Scheme II). Rate-determining allylic C-H abstraction to form  $\pi$ -complex 5 is facilitated by initial olefin chemisorption on coordinately unsaturated Mo sites. Subsequent formation of  $\sigma$ -complex 1 weakens the resulting allylic C-H bond by the O atom in the  $\alpha$  position, resulting in a fast 1,4-shift with reduction of Mo (path a) to form cinnamaldehyde. Alternatively, heterolytic C-O bond cleavage in 1 (path b) forms a molybdate anion (6) and a 4-allylaryl cation (2), which upon ring closure and loss of a proton results in indene formation. Reoxidation of reduced sites by dissociative chemisorption of gaseous oxygen and diffusion of O<sup>2-</sup> through the oxide lattice regenerates the active site 7.<sup>20</sup>

The cinnamaldehyde-forming  $\alpha$ -hydrogen abstraction route (path a) will be favored by catalysts with a high concentration of Bi, the hydrogen-abstracting component,<sup>19</sup> and electron-withdrawing substituents X, which destabilize carbonium ion 2. This is in agreement with the observed decreasing order of cinnamaldehyde selectivity (Bi<sub>2</sub>MoO<sub>6</sub> > Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub> > MoO<sub>3</sub>; X = Cl > H > CH<sub>3</sub> > OCH<sub>3</sub>). The role of Bi in accelerating the analogous 1,4-hydrogen shift in the corresponding allyl molybdates generated in situ from allyl alcohol and bismuth molybdate catalysts has been previously observed.<sup>1</sup> The enhancement in cinnamaldehyde selectivity by pyridine without affecting the overall rate of oxidation can be explained by base-assisted allylic deprotonation of 1. Conversely, indene formation (path b) is favored by electron-donating substituents X and catalysts of low bismuth content. Thus, the rate-determining step (allylic hydrogen atom abstraction) is controlled by radical substituent effects (X = OCH<sub>3</sub> > Cl > CH<sub>3</sub> > H), while product distribution is controlled by ionic ones. Substituents which favor decomposition of the common intermediate 1 via path a (X = Cl > H > CH<sub>3</sub> >

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OCH<sub>3</sub>) enhance cinnamaldehyde formation, while those which favor path b (X = OCH<sub>3</sub> > CH<sub>3</sub> > H > Cl) increase indene selectivity.

In terms of the selective oxidation of propylene over bismuth molybdate catalysts, these results are consistent with and reinforce the mechanism formulated on the basis of previous studies.<sup>1a</sup> Rate-determining  $\alpha$ -hydrogen atom abstraction from propylene results in the  $\pi$ - and  $\sigma$ -allylic intermediates analogous to 5 and 1 in Scheme II. A fast second hydrogen abstraction leads to formation and subsequent desorption of acrolein. In the presence of ammonia, condensation with Mo=O sites in 7 forms imido species Mo=NH, which leads to formation of the analogous N- $\pi$  intermediate prior to the N- $\sigma$  allylic species, which is the acrylonitrile precursor.

### Conclusions

The selective oxidation of allylbenzene over bismuth molybdate catalysts at 320 °C produces cinnamaldehyde and indene as sole products at low conversion (<2.5%). Relative rates of selective oxidation of *p*-XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CH=CH<sub>2</sub> under these conditions decrease in the order X = OCH<sub>3</sub> > Cl > CH<sub>3</sub> > H (radical substituent effects), while the X-indene-indene selectivity ratio in any

pair-wise run decreases in the order OCH<sub>3</sub> > CH<sub>3</sub> > H > Cl (cationic substituent effects). Formation of cinnamaldehyde and indene proceeds via a  $\pi$ -allyl radical surface complex formed in the rate-determining step, which undergoes C-O bond formation to give  $\sigma$ -O-allyl molybdate 1 (Scheme II). Indene is produced by ring closure of the phenyl allylcarbonium ion, which results from heterolytic C-O cleavage of 1. This process is favored by electron-donating groups X and catalysts of low  $\alpha$ -hydrogen-abstrating strength (low Bi). Cinnamaldehyde is formed by 1,4-hydrogen shift in 1, a process favored by electron-withdrawing X groups, catalysts of high H-abstrating strength (i.e., high Bi) and the presence of base.

By analogy, in selective oxidation and ammoxidation of propylene, the  $\pi$ -allylic surface complex is also radical-like. After conversion to the corresponding  $\sigma$ -O and  $\sigma$ -N allylic species, acrolein and acrylonitrile are formed, respectively.

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**Registry No.** Allylbenzene, 300-57-2; *p*-allylanisole, 140-67-0; *p*-allylchlorobenzene, 1745-18-2; *p*-allyltoluene, 3333-13-9; MoO<sub>3</sub>, 1313-27-5; Bi<sub>2</sub>Mo<sub>3</sub>O<sub>12</sub>, 13595-85-2; Bi<sub>2</sub>MoO<sub>6</sub>, 13565-96-3.

## $\alpha$ -Keto Acid Dehydrogenases: A Chemical Model

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A model system for the involvement of lipoic acid in  $\alpha$ -keto acid dehydrogenase systems is described. 2-( $\alpha$ -Hydroxyethyl)-3-benzyl-4-methylthiazolium tetrafluoroborate (6) serves as precursor for an analogue of the thiamine-bound active aldehyde 1 in the natural system. The model active aldehyde 7 reacts with linear disulfides, yielding thiols and thioesters. The 1,2-dithiolane, methyl lipoate (14), is unreactive under model reaction conditions. The tetrahedral intermediate which would be formed from methyl lipoate (14) plus an active aldehyde analogue 19 has been generated in a nonbiomimetic fashion. The synthetic tetrahedral intermediate 17 undergoes the reverse of the biological, disulfide reductive cleavage reaction.

The  $\alpha$ -keto acid dehydrogenases<sup>3,4</sup> mediate the production of energy-rich thioesters of coenzyme A (e.g., acetyl coenzyme A, 5, Scheme I) by oxidative decarboxylation of  $\alpha$ -keto acids (e.g., pyruvate). Our preliminary report<sup>5</sup> of a model system for the formation of thioesters catalyzed

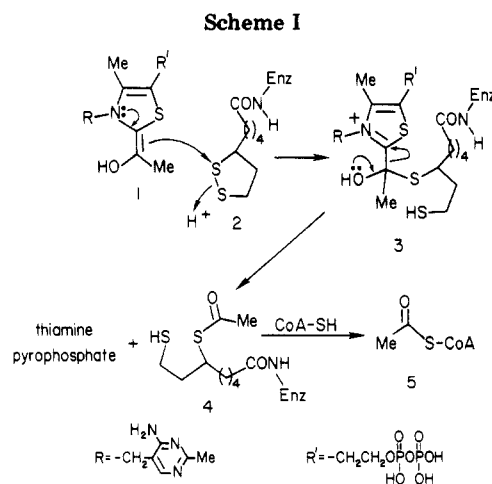
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by these enzyme systems supported the direct reductive acylation steps (1 + 2  $\rightarrow$  3  $\rightarrow$  4)<sup>6</sup> depicted in Scheme I. We were unable, however, to directly address the involvement of the 1,2-dithiolane, lipoic acid (see 2), in the biological

(6) The direct reductive acylation of Scheme I was suggested by Breslow (*Ann. N.Y. Acad. Sci.* 1962, 98, 445) and by White and Ingraham (*J. Am. Chem. Soc.* 1962, 84, 3109).